PATENT COOPERATION TREATY

12 MAY 2005

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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ENTERED ON INPROMA
12 MAY 2005

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	10.05.2005
Applicant's or agent's file reference PO104PCT/MCG	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/IE2004/000028	27.02.2004	28.02.2003

Applicant
GAS SENSORS SOLUTIONS LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:	Authorized Officer
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Form PCT/IPEA/416 (January 2004)

PATENT COOPERATION TREATY

PCT 10/547065

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PO104PCT/MCG	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/IE2004/000028	International filing date *(day/month/year)* 27.02.2004	Priority date *(day/month/year)* 28.02.2003

International Patent Classification (IPC) or national classification and IPC
G01N21/64

Applicant
GAS SENSORS SOLUTIONS LIMITED et al.

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 12 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 5 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the opinion
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☒ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☒ Box No. VI Certain documents cited
   - ☒ Box No. VII Certain defects in the international application
   - ☒ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
15.12.2004	10.05.2005

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IE2004/000028

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1-24	as originally filed
Claims, Numbers	
1-32	received on 15.09.2004 with letter of 13.09.2004
Drawings, Sheets	
1/10-10/10	as originally filed

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IE2004/000028

Box No. IV Lack of unity of invention

1. ☐ In response to the invitation to restrict or pay additional fees, the applicant has:
   - ☐ restricted the claims.
   - ☐ paid additional fees.
   - ☐ paid additional fees under protest.
   - ☐ neither restricted nor paid additional fees.

2. ☒ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

   ☐ complied with.

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

   ☒ all parts.

   ☐ the parts relating to claims Nos. .

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-32
	No:	Claims	
Inventive step (IS)	Yes:	Claims	22-32
	No:	Claims	1-21
Industrial applicability (IA)	Yes:	Claims	1-32
	No:	Claims	

2. Citations and explanations (Rule 70.7):

   see separate sheet

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IE2004/000028

Box No. VI Certain documents cited

1. Certain published documents (Rule 70.10)

   and / or

2. Non-written disclosures (Rule 70.9)

   see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item IV

Lack of unity of invention

This Authority considers that there are 2 inventions covered by the claims indicated as follows:

I: Claims 1-21 directed to a CO_2 sensor and to a method of making such a sensor, wherein the sensor comprises a pH indicator and a long-lived reference luminophore, said pH indicator being immobilized in a sol-gel matrix.

II: Claims 22-32 directed to a gas-sensitive sensor and a method of making such a sensor, wherein the sensor comprises a substrate having a sol-gel matrix containing a gas sensitive indicator printed thereon.

The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

a) Inventions I and II have the following feature in common: a gas sensitive sensor comprising a sol-gel matrix containing a gas sensitive indicator. This feature, however, is not new (cf. D1, page 1479, section "Membrane preparation") and can therefore not form the single general inventive concept.

b) Invention I differs from the disclosure of D1 in that the reference luminophore is doped in sol-gel particles or is immobilised in a separate oxygen impermeable layer whereas in D1 it is doped in nano-beads.

The technical problem to be solved by invention I may therefore be seen in providing alternative ways of incorporating the reference luminophore into the sensor.

Invention II differs from the disclosure of D1 in that the sol-gel matrix is printed onto the substrate whereas in D1 it is spin-coated.

The technical problem to be solved by invention II may therefore be seen in providing an alternative way of applying a sol-gel layer to a substrate.

Thus, the problems to be solved by inventions I and II are completely independent from each other and can therefore not provide a single general inventive concept.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

   D1: von Bültzingslöwen C et al., "Sol-gel based optical carbon dioxide sensor employing dual luminophore referencing for application in food packaging technology", Analyst, 127(11), 1478-1483, November 2002.
   D2: DE 198 29 657 A1
   D3: Klimant I and Wolfbeis S O: "Oxygen-Sensitive Luminescent Materials Based on Silicone-Soluble Ruthenium Diimine Complexes", Analytical Chemistry, 67(18), 3160-3165), September 15, 1995.
   D4: MacCraith B D et al.: "Fibre Optic Oxygen Sensor Based on Fluorescence Quenching of Evanescent-wave Excited Ruthenium Complexes in Sol-Gel Derived Porous Coatings", Analyst, 118, 385-388, April 1993.
   D5: Malins C et al., "Multi-analyte optical chemical sensor employing a plastic substrate", Meas. Sci. Technol., 11, 1105-1110, 2000.

2. **Invention I**

2a. **Claim 1**

Document D1 describes a CO_2 sensor comprising a pH indicator (HPTS) and a long-lived reference luminophore ($Ru(dpp)_3^{2+}$), wherein the reference luminophore is doped in nano-beads and co-immobilised with the pH indicator in a porous sol-gel matrix spin-coated onto a polymer substrate (cf. page 1479, sections "Reagents" and "Membrane preparation").

The first alternative of claim 1 differs from the sensor of D1 in that the reference luminophore is doped in sol-gel particles.

The second alternative of claim 1 differs from the sensor of D1 in that the reference luminophore is immobilised in a separate oxygen impermeable layer.

A technical problem may therefore be seen in providing alternative ways of incorporating the reference luminophore into the sensor.

Document D2 describes chemical sensors, e.g., CO_2 sensors, comprising a short-lived fluorescent dye sensitive to the analyte to be investigated and a long-lived reference luminophore (e.g., $Ru(dpp)_3^{2+}$/HPTS, cf. page 3, lines 65-66), wherein the reference luminophore is provided in an inert manner (cf. page 3, lines 33-35), e.g., by doping it in sol-gel particles and co-immobilising it with the short-lived fluorescent dye in the sensitive layer (cf. page 4, lines 19-20; figure 6.2) or by immobilising it in a separate impermeable layer (cf. page 4, line 16; figure 6.1: layer B) with the sensor layer containing the short-lived fluorescent dye (cf. figure 6.1: layer A) being laid over the impermeable layer.

Note: In D2 the the luminophore is immobilised in a lump of sol-gel glass which is then sintered and ground, i.e., in the end luminophore-doped sol-gel particles are obtained.

When confronted with the above problem, the skilled person would envisage applying this teaching of D2 to the sensor of D1, thereby arriving at both alternatives of claim 1 without the exercise of inventive skill (Article 33(3) PCT).

2b. **Claim 7**

Claim 7 is directed to a combination of a CO_2 sensor according to claim 1 and an O_2 sensor comprising an oxygen sensitive luminescent complex immobilised in a porous sol-gel matrix.

As already stated in paragraph 2a above the CO_2 sensor according to claim 1 is not considered to be inventive over D1 in combination with D2.

D1 states that the CO_2 sensor disclosed therein can be interrogated using the same

phase fluorimetric measurement technology that is used in lifetime-based oxygen sensing (cf. page 1483, last paragraph), which points towards combining the two sensors. D2 suggests arrays of sensors for different analytes using the same long-lived reference luminophore (cf. page 5, lines 37-39).

Document D5 describes a combined O_2/CO_2 sensor fabricated from dye-doped sol-gel spin-coated on thin glass films (cf. page 1105, right column, last paragraph), the O_2 sensor comprising an oxygen sensitive luminescent complex ($Ru(dpp)_3Cl_2$) doped in a sol-gel layer.

The subject-matter of claim 7 is therefore considered to be obvious in view of D1 in combination with D2 (for the CO_2 sensor) and D5 (for the combination with the O_2 sensor and the O_2 sensor as such).

2c. **Claim 13**

Document D1 describes a method of making a CO_2 sensor comprising suspending $Ru(dpp)_3^{2+}$ doped nano-beads in a co-immobilisation matrix solution, mixing the matrix solution into a pH indicator solution which comprises a pH indicator (HPTS) in a quaternary ammonium hydroxide solution (CTA-OH solution), saturating the mixture with CO_2 followed by deposition onto a substrate (cf. page 1479, section "Membrane preparation").

The method according to claim 13 differs from this disclosure in that it further comprises the steps of
(a) synthesis of a $Ru(dpp)_3(TSPS)$ ion-pair comprising mixing dissolved $Ru(dpp)_3Cl_2$ with trimethylsilylpropane sulfonic acid and sodium salt and allowing the ion-pair to precipitate, and
(b) synthesis of $Ru(dpp)_3^{2+}$ doped particles comprising condensing the dissolved $Ru(dpp)_3^{2+}(TSPS)_2$ ion-pair with TEOS and halting the condensation reaction with alcohol, washing the condensate with alcohol and drying the condensate.

A technical problem may therefore be seen in providing a method of synthesising $Ru(dpp)_3^{2+}$ doped particles.

As already stated in paragraph 2a above, doping the reference luminophore in sol-gel particles is suggested by D2. The synthesis of the $Ru(dpp)_3(TSPS)_2$ according to step (a) is known from document D3 (cf. page 3161, left column, section "Syntheses of Silicone-Soluble Ruthenium Complexes"). D3 furthermore suggests incorporation of Ruthenium Complexes in sol-gels giving document D4 as a reference (cf. page 3160, right column, second paragraph), which discloses the synthesis according to step (b) (cf. page 386, right column, second paragraph).

The method according to claim 13 is therefore considered to be obvious in view of D1 in combination with D2-D4 (Article 33(3) PCT).

2d. **Claim 14**

The method according to claim 14 is obvious in view of D1 in combination with D2 (see paragraph 2a above).

2e. **Dependent claims**

The following dependent claims do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step, the reasons being as follows:

claim 2:	cf. D1, page 1479, section "Membrane preparation"; cf. D2, page 3, line 66
claim 3:	cf. D1, page 1479, sections "Reagents" and "Membrane preparation"; cf. D2, page 3, line 66
claim 4:	cf. D1, page 1479, section "Membrane preparation"; cf. D4, page 386, right column, second paragraph
claims 5,6,8:	see claim 1 (Claim 8 was assumed to be dependent on claim 7 because otherwise the pH indicator and the long-lived reference luminophore would lack antecedence.)
claim 9:	cf. D4, page 386, right column, second paragraph;

cf. D5, page 1106, right column, lower half
(It was assumed that claim 9 reads as follows: "A combined O_2/CO_2 sensor as claimed in claim 7 or claim 8 wherein the oxygen sensitive luminescent complex is selected from the group comprising ruthenium-based compounds ...")

claims 10-12: cf. D5, page 1105, right column, last paragraph

claim 15: cf. D1, page 1481, left column, second paragraph

claim 16: cf. D1, page 1479, section "Membrane preparation";
cf. D2, page 3, lines 66-68

claims 17-19: cf. D1, page 1478 and page 1479, section "Membrane preparation"

3. **Invention II**

None of the documents cited in the International Search Report appears to disclose or fairly suggest the formation of a gas sensitive sensor by printing a sol-gel matrix containing a gas sensitive indicator onto a substrate.

The method according to independent claim 22 and its dependent claims 23-30 and the substrate according to independent claim 31 and its dependent claim 32 are therefore considered to be new and inventive over the available prior art.

Re Item VI
Certain documents cited

Non-written disclosures

Kind of non-written disclosure	Date of non-written disclosure *(day/month/year)*	Date of written disclosure referring to non-written disclosure *(day/month/year)*
Conference Opto-Ireland 2002: Optics and Photonics Technologies and Applications, Galway, Ireland	5-6/09/2002	03/2003 (Proc. SPIE, Vol. 4876, pages 806-815)

Re Item VII

Certain defects in the international application

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D5 is not mentioned in the description, nor are these documents identified therein.

Re Item VIII

Certain observations on the international application

1. In claim 7 the passage "the sensor being interrogatable ... is measured" specifies the optical reader. It is not clear which additional structural technical features of the sensor shall be thereby specified (Article 6 PCT). This passage is therefore not considered to limit the scope of the claim.

   Furthermore, claim 7 comprises all technical features of independent claim 1 and is therefore in fact dependent on claim 1. According to Rule 6.4(a) PCT this requires a reference to claim 1 in claim 7.

2. Claim 8 has been drafted as an independent claim. The terms "*the* pH indicator" and "*the* long-lived reference fluorophore" therefore lack antecedence, thereby rendering the claim unclear (Article 6 PCT).

   Furthermore, also in the following claims, which are dependent on claim 8, the following terms lack antecedence (Article 6 PCT):

   claim 9: *the* ruthenium-complex
   claim 10: *the* immobilised O2 sensor; *the* immobilised CO2 sensor; *the* substrate
   claim 11: *the* two sensors
   claim 12: *the* substrate

3. The dependencies of claims 12 and 21 are not correct, thereby rendering the claims unclear (Article 6 PCT).

4. A colorimetric-based sensor as claimed in claim 30 does not appear to be supported by the description, which consistently describes luminophore-based sensors (Art. 6 PCT).

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Claims

1. A CO_2 sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.

2. A CO_2 sensor as claimed in claim 1 wherein the pH indicator is selected from the group consisting of pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.

3. A CO_2 sensor as claimed in claim 1 or 2 wherein the long-lived reference luminophore is selected from the group consisting of a luminescent complex, in particular [Ru^{II}-tris(4,7-diphenyl-1,10-phenanthroline)]Cl_2, ruthenium-based compounds with α-diimine ligands, luminescent transition metal complexes with platinum metals Ru, Os, Pt, Ir, Re or Rh as the central metal atom and with α-diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.

4. A CO_2 sensor as claimed in any preceding claim wherein the porous sol-gel matrix is selected from the group consisting of a methyltriethoxysilane (MTEOS) sol-gel matrix, hybrid (organic-inorganic) sol-gel matrices including ethyltriethoxysilane (ETEOS), phenyltriethoxysilane (PhTEOS), n-octyl TEOS and methyltrimethoxysilane (MTMS), and UV-curable sol-gels, soluble ormosils, or hybrid polymer matrices.

5. A CO_2 sensor as claimed in any preceding claim wherein the luminophore is a ruthenium-doped sol-gel particle, in particular [Ru^{II}-tris(4,7-diphenyl-1,10-phenanthroline)]Cl_2- -doped particles.

6. A CO_2 sensor as claimed in any preceding claim wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a sol-gel matrix.

7. A combined O_2 /CO_2 sensor comprising:-

(a) an O_2 sensor comprising an oxygen sensitive luminescent complex immobilised in a porous sol-gel matrix, and

(b) an CO_2 sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer,

~~wherein~~ the sensor being interrogatable by an optical reade wherein the phase difference of a reference and an excitation

8. A combined O_2 /CO_2 sensor wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a porous sol-gel matrix. phase signa is measurec

9. A combined O_2 / CO_2 sensor as claimed in claim 8 wherein the ruthenium-complex is selected from the group consisting of an oxygen sensitive luminescent complex such as ruthenium-based compounds with α-diimine ligands and luminescent transition metal complexes with platinum metals (Ru, Os, Pt, Ir, Re or Rh) as the central metal atom and with α-diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.

10. A combined O_2 / CO_2 sensor as claimed in claim 8 or claim 9 wherein the immobilised O_2 sensor and the immobilised CO_2 sensor are coated onto the same substrate.

11. A combined O_2 / CO_2 sensor as claimed in claim 8 to 10 wherein the two sensors are coated onto the substrate side-by-side.

12. A combined O_2 / CO_2 sensor as claimed in any of claims 5 to 8 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate

materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.

13. A method of making a CO_2 sensor comprising :-

(1) synthesis of an $Ru(dpp)_3(TSPS)_2$ ion-pair comprising mixing dissolved $Ru(dpp)_3Cl_2$ with trimethylsilylpropane sulfonic acid, sodium salt and allowing the ion-pair to precipitate,

(2) synthesis of the particles comprising condensing the dissolved $Ru(dpp)_3(TSPS)_2$ ion-pair with TEOS and halting the condensation reaction with alcohol, washing the condensate with alcohol and drying the condensate, and

(3) and fabrication of the CO_2 sensor films comprising ~~either (a.)~~ suspending the doped reference particles in the coimmobilisation matrix solution, mixing the coimmobilisation matrix solution into a pH indicator solution which comprises a pH indicator in a quaternary ammonium hydroxide solution, and saturating the mixture immediately with CO_2 followed by deposition onto a substrate ~~or~~ (b.) a dual-layer configuration where in a low oxygen-sensitivity ruthenium complex is sealed in an oxygen impermeable layer and over-coated with the HPTS-based CO_2 sensing layer.

14. A method of making a CO_2 sensor in

15 ~~14.~~ A method as claimed in claim 13 wherein the quaternary ammonium hydroxide is selected from the group consisting of cetyl-trimetyl ammonium hydroxide (CTA-OH), tetra-octyl ammonium hydroxide (TOA-OH) or tetra-butyl ammonium hydroxide (TBA-OH) or other quaternary ammonium hydroxides.

16 ~~15.~~ A method as claimed in claim 13 or 15 wherein the pH indicator is selected from the group consisting pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.

17 ~~16.~~ A packaging medium having a combined CO_2 sensor and an O_2 sensor as claimed in any of claims 8 to 12 formed on a surface of the medium which will lie internally of the package when the package is formed.

18 ~~17~~. A packaging medium as claimed in claim ~~16~~ 17 wherein the sensors are formed on the packaging medium by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.

19 ~~18~~. A quality control method comprising reading a combined O_2 / CO_2 sensor as claimed in any of claims 8 to 12, formed on the internal surface of a package, with an optical reader, and determining the levels of O_2 and CO_2 inside the package in relation to a control.

20 ~~19~~. A method of screen-printing a combined O_2 /CO_2 sensor as claimed in any of claims 8 to 12 onto a substrate comprising forcing the sensor sol through a mask or mesh and drying the substrate.

21 ~~20~~. A method of ink-jet printing a combined O_2 /CO_2 sensor as claimed in any of claims 5 to 9 onto a substrate comprising filling an ink reservoir of an ink-jet printer with sensor sol and printing the sensor sol onto the substrate using an ink-jet printer.

22 ~~21~~. A method of forming a gas-sensitive sensor on a substrate comprising ~~coating or~~ printing the substrate with a porous sol-gel matrix comprising a gas sensitive indicator.

23 ~~22~~. A method as claimed in claim ~~21~~ 22 wherein the gas sensitive indicator is an oxygen-sensitive luminescent complex.

24 ~~23~~. A method as claimed in claim ~~21~~ 22 wherein the gas sensitive indicator is a pH indicator and a long-lived reference luminophore.

25 ~~24~~. A method as claimed in claim ~~21~~ 22 wherein the gas sensitive indicator is a pH indicator and the substrate is further provided with separate oxygen impermeable layer comprising a long-lived reference luminophore.

26 ~~25~~. A method as claimed in any of claims ~~21~~ 22 to ~~23~~ 24 wherein two gas sensors are formed on the substrate.

27 ~~26~~. A method as claimed in any of claims 22 ~~21~~ to 26 ~~25~~ wherein the sensor is formed on the substrate by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.

28 ~~27~~. A method as claimed in any of claims 22 ~~21~~ to 27 ~~26~~ wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.

29 ~~28~~. A method as claimed in any of claims 22 ~~21~~ to 28 ~~27~~ wherein the sensor is a luminophore-based sensor.

30 ~~29~~. A method as claimed in any of claims 22 ~~21~~ to 28 ~~27~~ wherein the sensor is a colorimetric-based sensor.

31 ~~30~~. A substrate having a gas-sensitive sensor formed thereon wherein the sensor comprises a sol-gel matrix comprising a gas sensitive indicator and the sensor has been formed by printing ~~or coating~~.

32 ~~31~~. A substrate as claimed in claim 31 ~~30~~ wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic cap.